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Ag^+ transfer across the water/1,2-dichloroethane interface facilitated by complex formation with tetraphenylborate derivatives

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Abstract

The assisted transfer of silver ion, Ag^+, by complexation of Ag^+ with the tetrakis(4-chlorophenyl)borate ($TPBCl^-$) anion was studied at the interface between two immiscible electrolyte solutions (ITIES).

The elucidation of the interfacial mechanisms employed the cyclic voltammetry technique applied to macro and micro liquid/liquid interfaces. This procedure allowed to identify Ag^+ as the species which is transferred at the liquid/liquid interface and also the formation of an 1:2 metal:ligand complex when $TPBCl^-$ is in excess.

The value for the formal transfer potential of silver(I) from aqueous to 1,2-dichloroethane was evaluated and the association constant for the $[Ag(TPBCl)_2]^-$ complex was determined.

Keywords: Silver ion; Tetrakis(4-chlorophenyl)borate anion; Liquid/liquid interfaces; Complex formation; Metal ion electroassisted recovery

1. Introduction

Silver has long been an important metal in society. It is valued for its resistance to corrosion and for its use in alloys and jewellery. Several processes are discussed in the literature for the recovery of silver [1,2], however its economic and environmental relevance constitutes a motivation for the development of improved methods of recovery. Several studies have been carried out using electrified liquid/liquid interfaces (interface between two immiscible electrolyte solutions (ITIES)). Combining the classical solvent extraction with electrochemical techniques can greatly improve the performance of the metal ion separation in particular at water/1,2-dichloroethane (DCE) and water/nitrobenzene (NB) interfaces, and a large number of papers can be found in the literature just in the last 10 years [3–11]. The electroassisted separation has been considered as potentially important in the field of waste solutions containing metal ion in particularly as a recovery process.

The driving force of the electroassisted transfer process is based on the Gibbs energy of ionic transfer of the metals or their complexes between two immiscible liquid phases: the interface between two immiscible electrolyte solutions (ITIES) can be polarised using an external source, creating a polarisation interval, where it is possible to observe the direct transfer of the metal ion if the supporting electrolytes have higher Gibbs energy of transfer than the metal. The Gibbs energy of transfer can be greatly reduced by promoting the complexation of the metal ion with a hydrophobic ligand [12].

In recent years the use of supported liquid membrane systems have been regarded as a valuable method for selective transport of Ag(I) using cyclic or acyclic ligands [13–16], protonated ionophores [17] or even polymers [18].

The earlier work of Hundhammer et al. [19], related to the electroassisted transfer of Ag^+, showed that the organic electrolyte tetraphenylborate (TPB^-) could react with silver

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ions promoting the transfer of silver ion across the water/NB interface by ion association and precipitation with TPB^-.

The results pointed out the need to consider the chemical reactivity of the organic electrolytes commonly employed in ion-transfer studies. This is particularly important in the case of the tetraphenylborate anion, which cannot be regarded as chemically inert. However other studies showed that when tetrakis(4-chlorophenyl)borate ($TPBCl^-$) was used as supporting electrolyte and nitrobenzene as organic phase no reaction was observed [20] more recent studies, also using nitrobenzene as organic solvent, seems to indicate that there is a stabilizing effect of $TPBCl^-$ on the silver ions [21].

The goal of the following study is to clarify the reaction process occurring at electrified water/DCE interface when silver ions are transferred in presence of TPB^- derivatives, i.e. tetrakis(4-chlorophenyl)borate or tetrakis(pentafluorophenyl)borate ($TPFPB^-$) a weakly coordinating anion.

2. Experimental

The experimental conditions used in this work are described in detail in preceding papers [22,23]. Briefly the current measured during cyclic voltammetry is by convention taken positive for the crossing of a positive charge from the water to the oil phase.

The Galvani potential difference between the water (w) and the organic (o) phases, $\Delta_o^w\phi$, defined as

$$\Delta_o^w\phi = \phi_w - \phi_o \quad (1)$$

was obtained by referencing the measuring cells using TMA^+ or ClO_4^- ions as internal standards [24]. The formal transfer potentials of these ions are +160 mV [25] and −170 mV [26], respectively.

The silver salts employed were $AgCH_3COO$ (Merck, p.a.), $AgNO_3$ (Merck, p.a.) and Ag_2SO_4 (Merck, p.a.). The aqueous supporting salts were $LiNO_3$ (Merck, p.a.) and Li_2SO_4 (Merck, p.a.). In some experiments the aqueous phase was buffered with equimolar concentrations of acetic acid (Merck, p.a.) and sodium acetate (Merck, p.a.), which also worked as supporting electrolyte.

In the organic phase the following supporting electrolytes were used:

- bis(triphenyl-phosphoranylidene) ammonium tetrakis(4-chlorophenyl)borate (BTPPATPBCl);
- bis(triphenyl-phosphoranylidene) ammonium tetrakis (pentafluorophenyl)borate (BTPPATPFPB);
- tetraoctylammonium tetraphenylborate (TOATPB), where BTPPATPBCl or BTPPATPFPB were prepared by metathesis of BTPPACl (Aldrich) and KTPBCl (Aldrich) or LiTPFPB (Boulder Scientific) and TOATPB was prepared as reported previously [24].

The electrochemical cells used throughout this work can be schematically represented as

Ag	AgCl	10 mM NaCl + 10 mM NaTPB (H_2O)	10 mM TOATPB (1,2-DCE)	‖	0.31 mM CH_3COOAg + 0.1 M (CH_3COOH/CH_3COONa) (H_2O)	AgCl	Ag	Cell I
Ag	AgCl	10 mM LiCl + 1 mM BTPPACl (H_2O)	*x* mM BTPPATPBCl (1,2-DCE)	‖	*y* mM CH_3COOAg + 0.1 M (CH_3COOH/CH_3COONa) (H_2O)	AgCl	Ag	Cell II
Ag	AgCl	10 mM TBACl (H_2O)	*x* mM TBATPBCl (1,2-DCE)	‖	*y* mM Ag NO_3 + 5 mM $LiNO_3$ (H_2O)		Ag	Cell III
Ag	AgCl	1 mM BTPPACl + 10 mM LiCl (H_2O)	*x* mM BTPPATPBCl (1,2-DCE)	‖	*y* mM Ag NO_3 + 5 mM $LiNO_3$ (H_2O)		Ag	Cell IV
Ag	AgCl	1 mM BTPPACl + 10 mM LiCl (H_2O)	*x* mM BTPPATPBCl + 5 mM BTPPATPFPB (1,2-DCE)	‖	*y* mM Ag $_2SO_4$ + 2.5 mM Li_2SO_4 (H_2O)	Ag_2SO_4	Ag	Cell V
Ag	AgCl	1 mM BTPPACl + 10 mM LiCl (H_2O)	*x* mM BTPPATPFPB (1,2-DCE)	‖	*y* mM Ag NO_3 + 5 mM $LiNO_3$ (H_2O)		Ag	Cell VI

Cells I, II and V have 0.22 cm^2 diameter, cells IV and V have 1.13 cm^2 diameter and for cell III different size micropipettes were used throughout the experiments. All experiments were performed at laboratory temperature (20 ± 2 °C).

3. Results and discussion

Fig. 1a shows the voltammogram obtained when an aqueous solution of Ag^+ is in the presence of excess TPB^- in the organic phase. The peak current decreases with increasing number of cycles becoming stable after ≈20 cycles. However at that time a precipitate is observed at the interface. Similar observations have been made for the water/NB interface [19] and were interpreted as indicative of simultaneous ion association and precipitation of Ag^+ by TPB^-.

The faradaic signal observed in presence of Ag^+ in the water phase and TPB^- in the organic phase was characterized by Hundhammer et al. [19] as quasi-reversible and led the authors to suggest the following four step process:

(1) transfer of TPB^- from the oil to the water phase;
(2) ion pairing between the metal ion and TPB^-;
(3) interfacial nucleation process;
(4) interfacial [AgTPB] film growth.

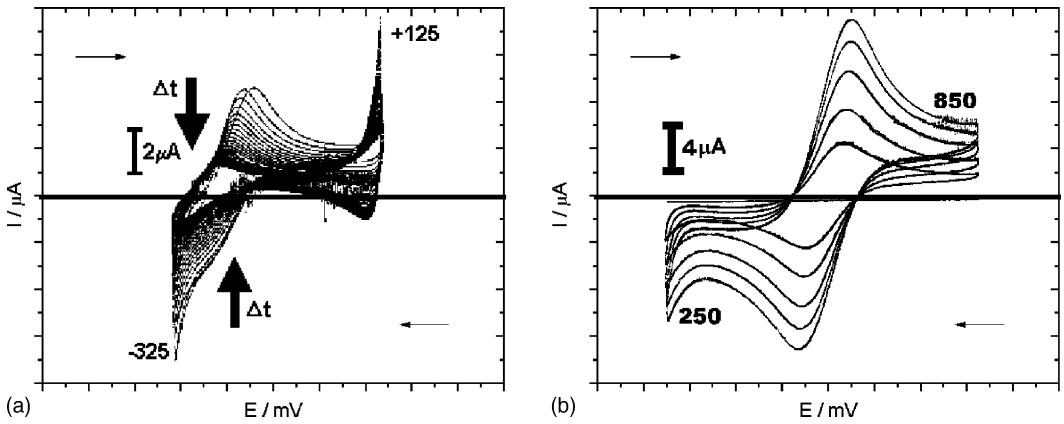

Fig. 1. Cyclic voltammograms obtained with (a) cell I: sweep rate = 50 mV s^{-1} and (b) cell II with $x = 10$ mM and $y = 0.31$ mM; sweep rate = 10, 25, 50, 75 and 100 mV s^{-1}.

When TPB^- is replaced by a more hydrophobic anion ($TPBCl^-$), a well defined reversible wave is observed in the cyclic voltammogram (Fig. 1b), a peak separation of 65 mV is obtained for sweep rates from 10 to 100 mV s^{-1}. The peak current is proportional to the square root of the sweep rate and the ratio between the forward and the reverse peak current intensity is close to 1. These observations indicate that the peaks in the cyclic voltammogram are due to a reversible, diffusion controlled transfer process of a single charged species. From this data a value of 8.1×10^{-6} cm^2 s^{-1} for the silver ion diffusion coefficient is obtained. This value is of the same order of magnitude of the results reported by Johans et al. [27].

Moreover, since $TPBCl^-$ is more hydrophobic than TPB^-, it is possible that in contrast with the proposal of Hundhammer et al. [19], the faradaic reversible signal observed is due to the transfer of the metal and not the transfer of the ligand. To discriminate between these two possibilities a set of experiments using micropipettes was carried out since the micropipette methodology is recognised to be a powerful tool to discriminate what species cross the interface [28].

One of the most important characteristics of micropipettes is the display of asymmetric diffusion regimes: spherical or linear, whether the transfer process is controlled by species entering (ingress) or leaving (egress) the micropipette, respectively. These two different processes can be easily distinguished during cyclic voltammetry experiments, as the egress transfer leads to a peak-shaped current response and the ingress results in a steady-state wave. Table 1 shows that the cyclic voltammograms should feature different shapes whether Ag^+ or $TPBCl^-$ ions transfer through the liquid interface and Ag^+ or $TPBCl^-$ is in concentration excess. It should be emphasized that this technique cannot be used to identify the complexation product which is therefore represented as $[Ag(TPBCl)_m]^{1-m}$.

Fig. 2 shows cyclic voltammograms obtained at micro-ITIES supported at the tip of micropipettes using different experimental conditions. When $TPBCl^-$ concentration is in excess (Fig. 2a) the cyclic voltammogram shows a peak on the forward scan and a steady-state wave on the reverse scan. These features correspond to a transfer limited by the ion present inside the pipette on the forward scan and the reverse current is limited by the diffusion of the product from the organic bulk to the liquid interface.

When Ag^+ concentration is in excess the cyclic voltammogram obtained is displayed in Fig. 2b and shows a steady-state wave both at the forward and reverse scans. This result corresponds to a transfer limited by the ion present outside the pipette, i.e. in the organic phase on the forward scan and the reverse current is limited by the ingress diffusion of the product towards the w/o interface.

Accordingly to Table 1 both results are compatible with the case where Ag^+ is the species crossing from the aqueous to the organic phase.

Experiments were also carried out when Ag^+ and $TPBCl^-$ are in equimolar conditions (voltammogram displayed in Fig. 2c). The cyclic voltammogram displays a steady-state wave at the forward scan and a peak-shaped voltammogram at the reverse scan. This result corresponds to a transfer limited by the ion present outside the pipette, i.e. in the organic phase on the forward scan and the reverse current is limited by the diffusion of the product from the aqueous phase towards the w/o interface. This result is indicative of $TPBCl^-$ species crossing from the organic to the aqueous phase.

A comparison between the results obtained in excess concentration (metal ion or organic anion) and in equimolar concentration seem at a first approach to be contradictory. In the first two cases the data shows that Ag^+ transfer is observed while when similar concentrations are used the results point to the transfer of $TPBCl^-$. In order to clarify the nature of the species formed between Ag^+ and $TPBCl^-$, different experiments were performed varying the concentration of $TPBCl^-$ in the organic phase either in the ligand or metal concentration excess case.

Table 1
Schematic representation of the diffusion regimes at a micro-liquid–liquid interface for the transfer of the metal ion or this of the anion

		Interfacial forward process	Interfacial reverse process	Resulting voltammogram
$TPBCl^-$ excess	Ag^+ transfer	Ag^+	$[Ag(TPBCl)_m]^{1-m}$	
	$TPBCl^-$ transfer	Ag^+	$[Ag(TPBCl)_m]^{1-m}$	
Ag^+ excess	Ag^+ transfer	$TPBCl^-$	$[Ag(TPBCl)_m]^{1-m}$	
	$TPBCl^-$ transfer	$TPBCl^-$	$[Ag(TPBCl)_m]^{1-m}$	

$TPBCl^-$ and Ag^+ excess cases are presented. The arrows represent the limiting diffusion process. The last column exhibits the shape of the resulting voltammogram for each case.

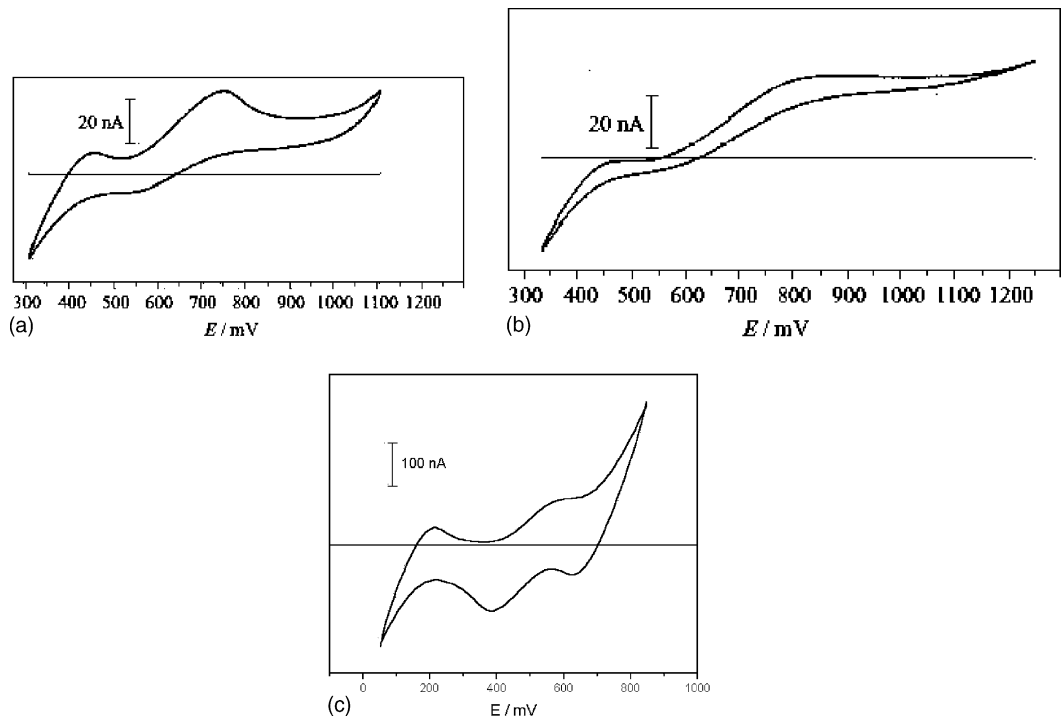

Fig. 2. Cyclic voltammogram obtained at micro liquid/liquid interfaces supported at the tip of micropipettes for the cases of excess of $TPBCl^-$ (a); excess Ag^+ (b); and quasi-equimolar concentrations (c) using cell III, respectively, with $x = 5$ mM; $y = 2.5$ mM and $x = 1$ mM; $y = 10$ mM and cell II with $x = 10$ mM; $y = 11$ mM. Sweep rate $= 50\ mV\ s^{-1}$.

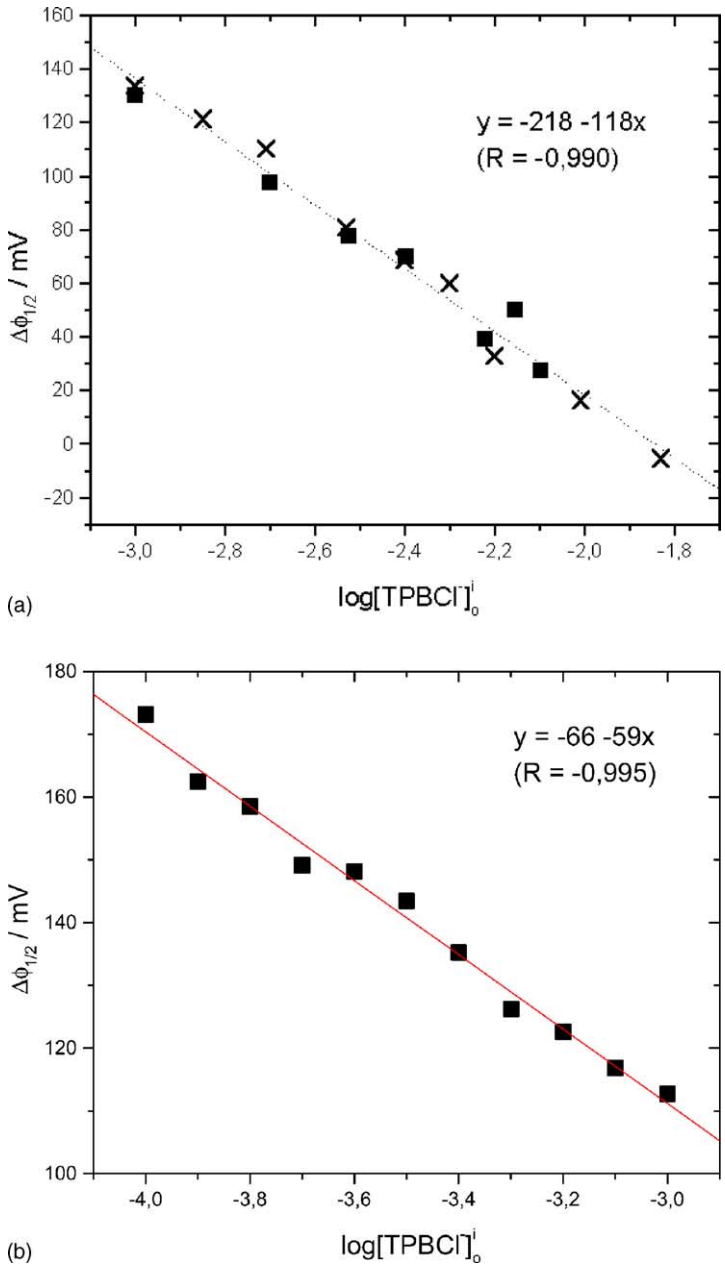

Fig. 3. Effect of $TPBCl^-$ concentration on the voltammetric behaviour of the Ag^+:$TPBCl^-$ complex. Analysis of the half-have potential dependence on both $TPBCl^-$ excess (a) and Ag^+ excess (b). Results obtained with (a) cell II (■) ($y = 0.31$ mM) and cell IV (×) ($y = 0.1$ mM); (b) cell V (···) ($y = 2.5$ mM). Sweep rate = 50 mV s^{-1}.

The results obtained from the analysis of the cyclic voltammograms are summarized in the plots of Fig. 3. The reproducibility of the data is well demonstrated since the plot obtained when the metal ion is the limiting concentration included data obtained independently in two different laboratories using two different concentrations of silver ion (Fig. 3a).

The assisted transfer of Ag^+ by tetrakis(4-chlorophenyl) borate anion is demonstrated by the linear dependence of the half-wave potential on the logarithm of concentration of the anion [29], with a slope of −118 mV (Fig. 3a) and −59 mV (Fig. 3b) in the $TPBCl^-$ and Ag^+ concentration excess situation, respectively.

Since the ligand assisting the transfer of Ag^+ is charged (anion) the theoretical treatment developed for the neutral ligand metal ion assisted transfer could not be, in principle, applied. However, recently, Tomaszewski et al. [30] analysed a theoretical model for the transfer of ions assisted by charged ligands in the form of ion pairs. The authors showed that the earlier results obtained for ion-transfer assisted by neutral ligands are also valid in the situation of charged ligands, namely for the concentration dependence

of the half-wave potential for the case of excess ligand concentration:

$$\Delta_o^w \phi_{1/2,[ML_j]^{z-j}} \propto -\frac{mRT}{zF} \ln c_{L^-}^o \quad (2)$$

and excess metal ion concentration:

$$\Delta_o^w \phi_{1/2,[ML_j]^{z-j}} \propto -\frac{RT}{zF} \ln c_M^w - \frac{(m-1)RT}{zF} \ln c_{L^-}^o \quad (3)$$

where m corresponds to the number of ligands (which in the present case has a -1 charge) and the other symbols have their usual meaning. We should stress that z is the charge of the transferring species which in the conditions of $TPBCl^-$ or Ag^+ large excess is the metal ion as reported previously.

Testing the results described earlier adjusting the model developed by Tomaszewski et al. [30] and summarized above show that in the previous experimental conditions Ag^+ ion is not transferred through the formation of an ion pair with $TPBCl^-$. However, if a reasonable extrapolation is made that Eqs. (3) and (4) are also valid for the case of the transfer of a charged complex between a metal ion and a negatively charged ligand, the results point out to the formation of a 1:2 complex between Ag^+ and $TPBCl^-$.

Further experiments lead to the results plotted in Fig. 4 for the Ag^+ ion concentration dependence of the half-wave potential. When changing the metal ion concentration, two distinct concentration domains are put in evidence and the transition point can be identified at a concentration ratio of $1Ag^+$:$2TPBCl^-$. This result is consistent with the previous one which supports the formation of the complex $[Ag(TPBCl)_2]^-$. From the analysis of Fig. 4 it is also possible to observe that when ligand concentration is in excess ($\log [Ag^+]_w < -3.4$) the half-wave potential is independent of silver ion concentration as predicted from Eq. (2).

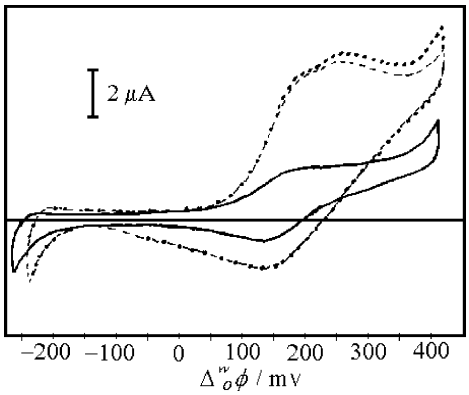

Fig. 5. Cyclic voltammogram registered in the experimental conditions of Fig. 4 for three different concentrations of silver ion 0.30 mM (—); 0.50 mM (- - -) and 0.63 mM (· · ·). Sweep rate = 50 mV s^{-1}.

However, when the metal ion concentration is closer to the $TPBCl^-$ concentration ($\log [Ag^+]_w > -3.4$) the formation of a precipitate can be observed at the interface and a second peak is visible at the voltammograms as can be confirmed in Fig. 5. Although there is an increase in the difficulty in data analysis for silver ion concentrations greater than 0.5 mM, the half-wave potential of the first peak is linearly dependent on the $\log [Ag^+]_w$ with a slope of 56 mV/decade as shown in Fig. 4.

Fig. 6 shows the dependence of the peak current on the silver ion concentration. In the lower silver ion

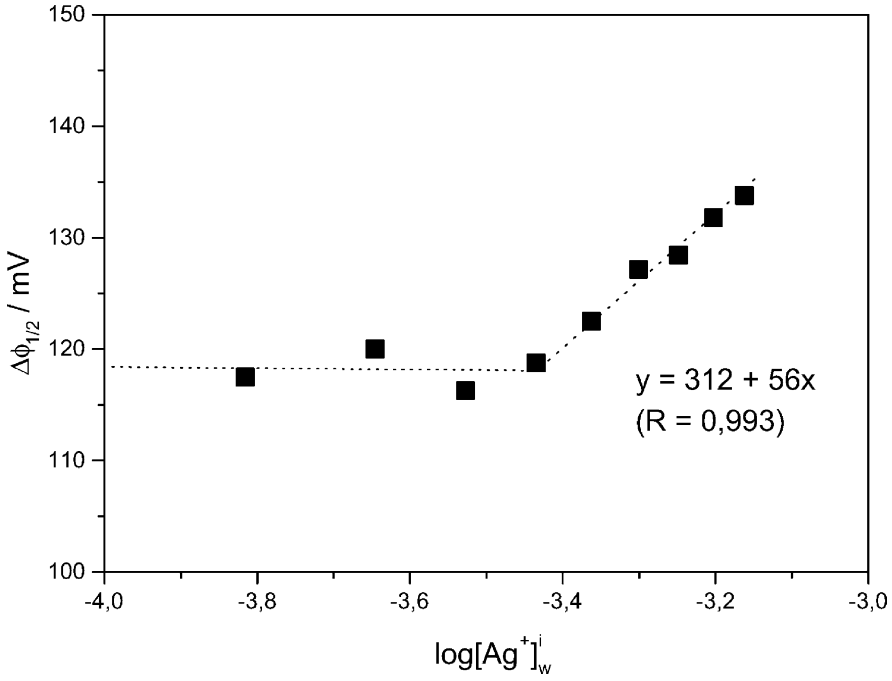

Fig. 4. Analysis of the half-have potential dependence on silver ion concentration when $TPBCl^-$ is kept in excess. Results obtained with cell II (x = 1.0 mM). Sweep rate = 50 mV s^{-1}.

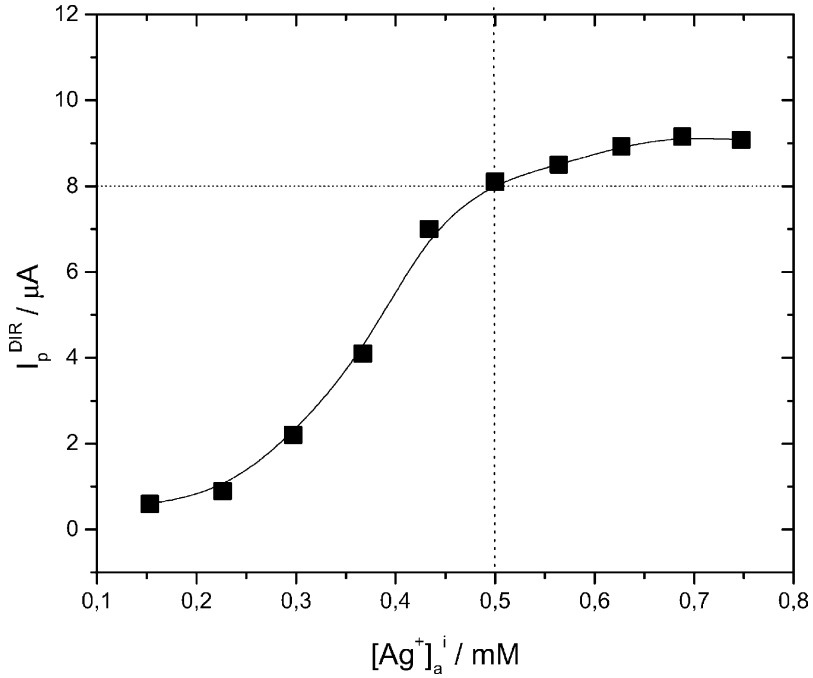

Fig. 6. Peak current dependence on silver ion concentration using the same experimental conditions of Fig. 4.

concentration region ($TPBCl^-$ excess), the increase in current with the $[Ag^+]_w$ can be explained by the formation of the $[Ag(TPBCl)_2]^-$ complex. Further increase of $[Ag^+]_w$ (for $[Ag^+]_w > 0.5$ mM) shows that no peak current saturation is reached, instead a further increase in current is observed. These observations may be rationalized by assuming the formation of the ion pair [Ag(TPBCl)] in the organic phase as described by Eq. (4).

$$[Ag(TPBCl)_2]^-(o) + Ag^+(w) \rightleftharpoons 2[Ag(TPBCl)](o) \quad (4)$$

For silver ion concentrations higher than 0.75 mM it was impossible to have a stable cyclic voltammogram since in this concentration domain the amount of precipitate was too large.

3.1. Evaluation of the association constant

Replacing tetrakis(4-chlorophenyl)borate by tetrakis (pentafluorophenyl)borate as the anion of the organic supporting electrolyte there is an increase of the current at the positive hand side of the polarisation window. When the potential limit is extended towards more positive potentials, it appears that this current rise corresponds to a reversible wave as exhibited in Fig. 7. Since the fluorine atoms are "harder" bases than chloride in the Pearson's classification [31] which does not favours the interactions with the "soft" metal ion, Ag^+ the increase in current can be attributed to the direct transfer of silver(I) ions, which allowed the determination of the formal transfer potential of silver(I) ($\Delta_o^w\phi^0_{Ag^+} = 497 \pm 6$ mV). Furthermore, Johans et al. [27] reports the use of $TPFPB^-$:Ag^+ electrochemical system. Although using a different $TPFPB^-$:Ag^+ molar ratio these authors do not report the formation of any peak which could be assigned to the $TPFPB^-$:Ag^+ complex formation.

With this value it is possible to estimate the value of the accumulative association constant β_2^0, corresponding to the formation in the organic phase of the complex $[Ag(TPBCl)_2]^-$. From the intercept of the line adjusted to data in Fig. 3a and b, the value for $\log \beta_2^0$ was estimated using the equations established by Reymond et al. [29], assuming $\xi = (D^o/D^w)^{1/2} = 1.12$ and $\Delta_o^w\phi^0_{Ag^+} = 497$ mV. The values obtained were, respectively, 12.1 and 11.8 which allow us to estimate the value of $\log \beta_2^0$ as 11.9.

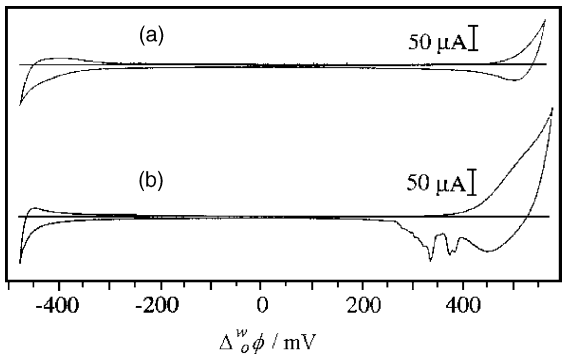

Fig. 7. Cyclic voltammogram registered in the absence (a) or in the presence (b) Ag(I) in the aqueous phase and BTPPATPFPB as the organic supporting electrolyte in DCE extending the available potential window towards more positive potentials. The experimental results were obtained using cell VI with $x = 2.5$ mM; $y = 0$ mM (a) or $y = 2.5$ mM (b) and sweep rate = 50 mV s^{-1}.

4. Conclusions

Voltammetry at micro-ITIES supported at micropipettes shows that, during the assisted transfer of Ag^+ by $TPBCl^-$, Ag^+ is the species crossing from the aqueous to the organic phase, regardless of the limiting process being the diffusion of the metal ion or the ligand towards the interface. This contrasts with the transfer process reported in the literature [19] when TPB^- is the ligand dissolved in the organic phase.

Analysis of voltammetric data obtained either in excess of anion or cation led us to propose a reaction scheme which involved as a first step the formation of a complex ion ($[Ag(TPBCl)_2]^-$). With the further increase on silver ion concentration there is the formation of ion pair ([Ag(TPBCl)]) with the consequent precipitation in the aqueous phase.

The apparent discrepancy of results obtained in the interpretation of the micropipette results may be rationalized if we consider that the formation of a rather large hydrophobic complex ion ($[Ag(TPBCl)_2]^-$) would be very unfavourable to occur in the aqueous phase therefore the formation of such complex ion will only be possible if the silver ion would cross to the organic phase. By contrast, although neutral, the ion pair [Ag(TPBCl)] can be formed in the aqueous phase (the visible formation of a precipitate is the proof of that) and therefore the crossing of $TPBCl^-$ would be required.

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